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METHOD FOR PRODUCING ANISOTROPIC OXIDE MAGNETIC POWDER AND METHOD FOR  
PRODUCING PLASTIC MAGNET  
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## 1. Title

Method for Producing Anisotropic Oxide Magnetic Powder and Method for Producing Plastic Magnet

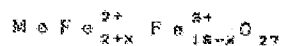
## 2. Claims

1. A method for producing an anisotropic oxide magnetic powder that comprises:

adding zinc oxide and/or a compound that, when heated, becomes zinc oxide to a raw-material powder comprised of iron oxide and an oxide of a minimum of one kind of metal selected from a group consisting of Ba, Sr, and Pb and/or a compound that becomes said oxide when heated;

blending and calcining said mixture; and

subsequently pulverizing and thermally treating the calcined product, thereby producing an anisotropic oxide magnetic powder having the following hexagonal crystal structure:



(M being one or more kinds of metals selected from a group consisting of Ba, Sr, and Pb and  $x = +0.05$  to  $-0.10$ ),

wherein, as the iron oxide,  $Fe_2O_3$  and  $Fe_3O_4$  are blended so as to set the molar ratio of  $Fe^{2+}$  to  $Fe^{3+}$  to  $1 - 1.05 : 8$ ,

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\* Number in the margin indicates pagination in the foreign text.

wherein the zinc oxide and/or the compound that becomes zinc oxide when heated is added in such a quantity that the Zn content becomes 1.0 to 10 mole % of  $\text{Fe}^{2+}$ , and

wherein the calcining is conducted at a temperature of from 1150 to 1250 °C under an oxygen partial pressure of from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  atm.

2. A method for producing plastic magnets comprising:

adding a resin to the anisotropic oxide magnetic powder stated in Claim 1,

kneading the mixture, and

molding said kneaded product while applying a magnetic field to it.

3. Detailed Description of the Invention

[Field of Industrial Application]

The present invention pertains to a method for producing an anisotropic oxide magnetic powder and a method for producing plastic magnets intended for electrical equipment and the like, using this magnetic powder.

[Related Art]

Heretofore, ferrite-based and rare earth-based sintered magnets and plastic magnets have been available as permanent magnets used in /2 electrical equipment and the like.

Plastic magnets have various advantages over sintered magnets. For instance, they have high dimensional accuracy, those having

complex shapes can be obtained easily, and they do not chip or crack easily. In addition, they are highly suitable for mass production. For these reasons, their production volume is increasing rapidly at present. These plastic magnets are compounds of mainly magnetic powder and polymeric resin, and oxide magnetic materials, such as Ba ferrite, Sr ferrite, and the like, are used as the magnetic powder. These are inexpensive and used in the largest quantities. These ferrites have the magnetoplumbite-type (M-type) hexagonal crystal structure, of which  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$  and  $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$  are especially suitable as permanent magnets, and all of the ferrites that are produced as permanent magnets are this M-type at present.

There is a demand for improved magnetic characteristics of plastic magnets, and there is a demand for an inexpensive powder that has better magnetic characteristics than those of the M-type ferrites. In JP-A-S57-18303 is disclosed a method for producing sintered permanent magnets using a hexagonal ferrite having a crystal structure called the W-type:  $\text{Me} \cdot \text{Fe} \cdot \frac{2}{3} \text{Fe} \cdot \frac{8}{3} \text{O}_{27}$  (Me being a metal selected from a group consisting of barium, strontium, and lead). Among the W-type ferrites,  $\text{Ba} \cdot \text{Fe} \cdot \frac{2}{3} \text{Fe} \cdot \frac{8}{3} \text{O}_{27}$  and  $\text{Sr} \cdot \text{Fe} \cdot \frac{2}{3} \text{Fe} \cdot \frac{8}{3} \text{O}_{27}$  exhibit excellent magnetic characteristics, and, compared with M-type hexagonal ferrites, their spontaneous magnetism is higher by about 10 %, and their anisotropy fields are approximately the same [F. K. Lotgering, etc.: J. Appl. Phys., 51 (1980), 5913].

However, because these W-type ferrites contain  $\text{Fe}^{2+}$ , they have a problem in that their production process requires complex ambience and temperature controls; in particular, in the calcining and sintering steps, complex ambience and temperature controls are required for the purpose of homogenizing the composition (forming a single phase comprised of a W-type ferrite and equalizing the  $\text{Fe}^{2+}$  concentration) and improving the sintered density.

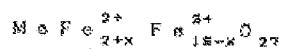
[Problems that the Invention Intends to Solve]

The present invention intends to provide a method for producing an anisotropic oxide magnetic powder that improves magnetic characteristics--especially remnant flux density and maximum energy product--inexpensively and advantageously and a method for producing plastic magnets using this magnetic powder.

[Means for Solving the Problems]

In view of the aforesaid problems, the present inventors conceived the idea of using W-type ferrites in place of M-type ferrites so as to improve the magnetic characteristics of magnetic powder inexpensively and easily, and they conducted extensive research to develop a magnetic powder production method and, as a result, achieved the method of the present invention. Further, the use of the magnetic powder produced by the method of the present invention for plastic magnets improves the magnetic characteristics of the plastic magnets.

Namely, the present invention pertains to a method for producing an anisotropic oxide magnetic powder that comprises: adding zinc oxide and/or a compound that, when heated, becomes zinc oxide to a raw-material powder comprised of iron oxide and an oxide of a minimum of one kind of metal selected from a group consisting of Ba, Sr, and Pb and/or a compound that becomes said oxide when heated; blending and calcining said mixture; and subsequently pulverizing and thermally treating the calcined product, thereby producing an anisotropic oxide magnetic powder having the following hexagonal crystal structure:



(M being one or more kinds of metals selected from a group consisting of Ba, Sr, and Pb and  $x = +0.05$  to  $-0.10$ ),

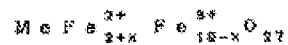
wherein, as the iron oxide,  $Fe_2O_3$  and  $Fe_3O_4$  are blended so as to set the molar ratio of  $Fe^{2+}$  to  $Fe^{3+}$  to 1 - 1.05 : 8, wherein the zinc oxide and/or the compound that becomes zinc oxide when heated is added in such a quantity that the Zn content becomes 1.0 to 10 mole % of  $Fe^{2+}$ , and wherein the calcining is conducted at a temperature of from 1150 to 1250 °C under an oxygen partial pressure of from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  atm, and

it also pertains to a method for producing plastic magnets comprising: adding a resin to the anisotropic oxide magnetic powder that is produced by the aforesaid method, kneading the mixture, and molding said kneaded product while applying a magnetic field to it.

[Operation]

The following will explain the present invention in detail.

As the raw-material powder used for producing the magnetic powder /3 of the present invention, an oxide of a minimum of one kind of metal selected from Ba, Sr, and Pb and/or a compound, such as a carbonate or the like, that becomes said oxide when heated as well as a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  as the iron oxide in quantities necessary for forming the W-type ferrite phase are used. For facilitating the formation of the W-type ferrite phase:



(Me: a metal selected from Ba, Sr, and Pb and  $x = +0.05$  to  $0.10$  [sic]), the addition of  $\text{Fe}_3\text{O}_4$  is one of the key points of the present invention, and it is added in a quantity that sets the molar ratio of the  $\text{Fe}^{2+}$  content to  $\text{Fe}^{3+}$  content to  $1 - 1.05 : 8$ . When the ratio is out of this range, the aforesaid W-type ferrite phase will not be formed.

Zn is added for the purpose of stabilizing the W phase. Zn is added in the form of zinc oxide and/or a compound that becomes zinc oxide when heated, but it is preferable to add it in the form of zinc oxide. The addition quantity of zinc is from  $1.0$  to  $10$  mole % of the  $\text{Fe}^{2+}$  content in the raw-material powder. If it is less than  $1.0$  mole %, it is not effective in stabilizing the W-type ferrite phase, and adding it in a quantity exceeding  $10$  mole % causes the magnetic characteristics to deteriorate.



The aforesaid raw-material powder ingredients are mixed and calcined. The mixing is carried out by an ordinary method, using a ball mill or the like.

Calcining is one of the key points of the present invention, and the calcining conditions are important for forming a W-type ferrite. That is, the calcining temperature is set to from 1150 to 1250 °C, and the oxygen partial pressure of the ambience is set to from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  atm. The oxygen partial pressure is especially important here, and, unless it is in the range of from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  atm, it is not possible to achieve the  $\text{Fe}^{2+}$  concentration that leads to the formation of a W-type ferrite single phase. In addition, if the calcining temperature is below 1150 °C, the ferrite formation reaction and grain growth do not progress sufficiently, while a temperature exceeding 1250 °C causes the sintering to progress excessively, and the product requires a large amount of time and energy to pulverize. The heating and cooling in the calcining step are preferably carried out at a temperature raising rate of approximately 200 °C/hour and a temperature cooling rate of approximately 1500 °C/hour.

The aforesaid calcined powder is pulverized and further subjected to a heat treatment for homogenization, thereby forming a magnetic powder.

The pulverization is carried out in an organic solvent, such as alcohol, toluene, methyl ethyl ketone (MEK), or the like, with a wet ball mill, and it is preferable to set the average particle size of

the obtained powder to from 0.6 to 1.0  $\mu\text{m}$  (according to the Fischer method). Since the single-domain particle size of hexagonal ferrites is approximately 1  $\mu\text{m}$ , an average particle size of 1  $\mu\text{m}$  or smaller is ideal.

Next, a heat treatment is carried out for the purpose of reducing crystal defects in this magnetic powder and homogenizing the W-type ferrite phase. The ambience for the heat treatment is an inactive gas, and the temperature of the heat treatment is preferably in the range of from 850 to 1000  $^{\circ}\text{C}$ . A temperature below 850  $^{\circ}\text{C}$  leads to poor heat-treatment efficiency, while a temperature exceeding 1000  $^{\circ}\text{C}$  causes the grain growth to progress excessively, thus increasing multi-domain particles. For the purpose of optimizing the particle distribution of the magnetic powder particles in the heat treatment, it is effective to add from 0.1 to 3 % by weight of silica ( $\text{SiO}_2$ ). The addition timing may be either before the calcining or immediately prior to the heat treatment.

The magnetic powder prepared by the aforesaid production method is mixed with a resin to produce plastic magnets. The resin here may be either a thermoplastic resin or thermosetting resin.

Thermoplastic resins that can be used here include vinyl chloride resins, vinylidene chloride resins, vinyl acetate resins, vinyl alcohol resins, vinyl acetal resins, methyl methacrylate resins, polystyrene resins, polyamide resins, polyethylene resins, polypropylene resins, fluororesins, and the like, and thermosetting

resins that can be used here include phenolic resins, epoxy resins, polyester resins, silicone resins, melanine [sic] resins, alkyd resins, polyfunctional vinyl copolymers, and the like. These may be used singly or in combination.

The compounding quantity of the resin is preferably from 40 to 28 % by volume in relation to other constituents. Incidentally, according to the objective, the magnetic powder may, as appropriate, be surface-treated with a coupling agent or the like to improve the wettability with the resin or incorporate a stabilizer, lubricant, or the like.

The kneading of the magnetic powder and resin as well as other ingredients can be implemented with a commonly used kneading machine, such as a twin screw extruder or the like. /4

The molding is carried out by applying a magnetic field to the aforesaid kneaded product while it is in a heated and melted state, thereby orienting the anisotropic oxide magnetic powder (ferrite particles), and subsequently by cooling and solidifying it, and the molding method employed here may be any known method, such as injection molding, compression molding, extrusion molding, or the like. The intensity of the applied magnetic field is 5000 Oersted (Oe) or higher, preferably 10000 Oe, better yet, 20000 Oe. The thus-obtained plastic magnet having excellent magnetic characteristics can be formed in various shapes and is expected to contribute to the field of electronics components and the like.

#### [Working Examples]

Using  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{ZnO}$ , and  $\text{BaCO}_3$  or  $\text{SrCO}_3$  powders, 5 kg of a raw-material powder was formulated according to each compounding condition, and this mixture was calcined.

Each calcined powder was formed into a slurry of a 50 % by weight concentration, using toluene, and pulverized with a wet ball mill, thereby forming a powder having an average particle size of 0.8  $\mu\text{m}$  (according to the Fischer method), after which the powder was dried and subsequently heat-treated. The compounding conditions, calcining conditions, and heat-treatment conditions of the raw materials are shown in Table 1, together with those of comparative examples.

Next, using the aforesaid heat-treated powders, plastic magnets were produced.

As the resin, polyamide resin (Nylon 12) was used, and the compounding quantity of the resin was set to 37 % by volume. After the resin and each of the aforesaid magnetic powders were mixed, the mixture was kneaded with a twin screw extruder, thereby forming pellets, and these pellets were molded in a magnetic field, using a magnetic-field injection molding machine, thereby obtaining an anisotropic plastic magnet.

The magnetic characteristics of the obtained plastic magnets were measured with a direct current B-H tracer, and the measured values are shown in Table 2, together with the results of the comparative examples.

The plastic magnets of the present invention all exhibited excellent magnetic characteristics.

TABLE 1-a

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
		組成	配合量	モル比	$Fe^{2+}/Fe^{3+}$	焙焼条件	熱処理条件	FeO分析値
		(g)	(g)		モル比			(m)
例	1	$Fe_2O_3$ $Fe_3O_4$ $BaCO_3$ $ZnO$ $SiO_2$ *	2950 1430 510 10 10	6 2 1 0.04	1/8	$O_2$ 濃度 (l) $1 \times 10^{-4}$ 気圧 (j) 温度 × 時間 (k) $1250^\circ C \times 4 Hr$	$O_2$ 濃度 (l) $1 \times 10^{-4}$ 気圧 (j) 温度 × 時間 (k) $1000^\circ C \times 1 Hr$	1.95 モル (l) (フェライト 1 モル中) $x = 0.05$
	2	$Fe_2O_3$ $Fe_3O_4$ $BaCO_3$ $ZnO$ $SiO_2$ *	2950 1430 510 28 10	6 2 1 0.1	1/8	$O_2$ 濃度 (l) $5 \times 10^{-4}$ 気圧 (j) 温度 × 時間 (k) $1150^\circ C \times 4 Hr$	$O_2$ 濃度 (l) $5 \times 10^{-4}$ 気圧 (j) 温度 × 時間 (k) $950^\circ C \times 1 Hr$	1.80 モル (l) (フェライト 1 モル中) $x = 0.10$
	3	$Fe_2O_3$ $Fe_3O_4$ $SrCO_3$ $ZnO$ $SiO_2$ *	3010 1480 490 27 10	6 2 1 0.1	1/8	$O_2$ 濃度 (l) $5 \times 10^{-4}$ 気圧 (j) 温度 × 時間 (k) $1200^\circ C \times 4 Hr$	$O_2$ 濃度 (l) $5 \times 10^{-4}$ 気圧 (j) 温度 × 時間 (k) $950^\circ C \times 1 Hr$	1.90 モル (l) (フェライト 1 モル中) $x = 0.10$
	4	$Fe_2O_3$ $Fe_3O_4$ $SrCO_3$ $ZnO$ $SiO_2$ *	3010 1480 490 27 10	6 2 1 0.1	1/8	$O_2$ 濃度 (l) $1 \times 10^{-3}$ 気圧 (j) 温度 × 時間 (k) $1150^\circ C \times 4 Hr$	$O_2$ 濃度 (l) $1 \times 10^{-3}$ 気圧 (j) 温度 × 時間 (k) $900^\circ C \times 1 Hr$	1.80 モル (l) (フェライト 1 モル中) $x = 0.10$
	5	$Fe_2O_3$ $Fe_3O_4$ $SrCO_3$ $ZnO$ $SiO_2$ *	3010 1480 490 27 10	6 2 1 0.1	1/8	$O_2$ 濃度 (l) $1 \times 10^{-3}$ 気圧 (j) 温度 × 時間 (k) $1150^\circ C \times 4 Hr$	$O_2$ 濃度 (l) $1 \times 10^{-3}$ 気圧 (j) 温度 × 時間 (k) $900^\circ C \times 1 Hr$	1.80 モル (l) (フェライト 1 モル中) $x = 0.10$
	6	$Fe_2O_3$ $Fe_3O_4$ $SrCO_3$ $ZnO$ $SiO_2$ *	3010 1530 490 28 10	6 2 1 0.1	1.05/8	$O_2$ 濃度 (l) $1 \times 10^{-3}$ 気圧 (j) 温度 × 時間 (k) $1200^\circ C \times 4 Hr$	$O_2$ 濃度 (l) $1 \times 10^{-3}$ 気圧 (j) 温度 × 時間 (k) $900^\circ C \times 1 Hr$	2.00 モル (l) (フェライト 1 モル中) $x = 0.00$

Key: a) working examples; b) composition; c) compounding quantity; d) molar ratio; e)  $Fe^{2+}/Fe^{3+}$  molar ratio; f) calcining conditions; g) heat-treatment conditions; h) FeO analytical value; i)  $O_2$  concentration; j) atm; k) temperature x time; l) mol; m) in 1 mol of ferrite

Note) \*: added prior to the heat treatment.

TABLE 1-b

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	組成 (b)	配合量 (g) (c)	モル比 (d)	Fe <sup>2+</sup> /Fe <sup>3+</sup> モル比 (e)	焼結条件 (f)	熱処理条件 (g)	FeO 分析値 (h)
(a) 比較例	1 Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> BaCO <sub>3</sub> ZnO SiO <sub>2</sub> *	2950 430 610 10 10	6 2 1 0.04	1/8	O <sub>2</sub> 濃度 (i) 1×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 1200℃×4hr	O <sub>2</sub> 濃度 (i) 1×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 1000℃×1hr	1.20 モル (l) (フェライト 1 モル中) x = -0.80 (m)
	2 Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> BaCO <sub>3</sub> ZnO SiO <sub>2</sub> *	2950 430 610 10 10	6 2 1 0.04	1/8	O <sub>2</sub> 濃度 (i) 5×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 1300℃×4hr	O <sub>2</sub> 濃度 (i) 5×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 930℃×1hr	0.80 モル (l) (フェライト 1 モル中) x = -1.20 (m)
	3 Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> BaCO <sub>3</sub> ZnO SiO <sub>2</sub> *	2950 430 610 130 10	6 2 1 0.6	1/8	O <sub>2</sub> 濃度 (i) 5×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 1300℃×4hr	O <sub>2</sub> 濃度 (i) 5×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 950℃×1hr	1.50 モル (l) (フェライト 1 モル中) x = -0.50 (m)
	4 Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> BaCO <sub>3</sub> ZnO SiO <sub>2</sub> *	2950 470 680 11 10	6 2 1 —	1/8	O <sub>2</sub> 濃度 (i) 1×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 1200℃×4hr	O <sub>2</sub> 濃度 (i) 1×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 900℃×1hr	1.60 モル (l) (フェライト 1 モル中) x = -0.40 (m)
	5 Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> BaCO <sub>3</sub> ZnO SiO <sub>2</sub> *	3100 1290 830 26 10	6.3 1.8 1 0.1	0.9/8	O <sub>2</sub> 濃度 (i) 1×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 1200℃×4hr	O <sub>2</sub> 濃度 (i) 1×10 <sup>-3</sup> 気圧 (j) 温度×時間 (k) 900℃×1hr	1.70 モル (l) (フェライト 1 モル中) x = -0.30 (m)
	6 Fe <sub>2</sub> O <sub>3</sub> BaCO <sub>3</sub> SiO <sub>2</sub> *	4150 860 10	6 1 —	0/8	O <sub>2</sub> 濃度 (i) 1 気圧 (j) 温度×時間 (k) 1300℃×4hr	O <sub>2</sub> 濃度 (i) 1 気圧 (j) 温度×時間 (k) 900℃×1hr	0 モル (l) M 型 フェライト (n)

Key: a) comparative examples; b) composition; c) compounding quantity; d) molar ratio; e) Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio; f) calcining conditions; g) heat-treatment conditions; h) FeO analytical value; i) O<sub>2</sub> concentration; j) atm; k) temperature × time; l) mol; m) in 1 mol of ferrite; n) M-type ferrite

Note) \*: added prior to the heat treatment.

TABLE 2

		残留磁束密度 (kG)	保磁力 (kOe)	配向度 (%)	(BH) max (MG Oe)
(a) 実 例	1	3.10	3.20	97.0	2.00
	2	3.00	3.00	97.0	1.96
	3	3.10	3.15	96.8	1.98
	4	3.00	3.00	97.0	1.96
	5	3.10	3.15	96.8	1.98
	6	3.15	3.15	97.0	2.05
(b) 比 較 例	1	2.00	2.50	90.0	1.10
	2	1.70	1.90	87.0	1.00
	3	2.30	2.60	92.0	1.30
	4	2.60	2.50	92.5	1.45
	5	2.60	2.50	92.0	1.45
	6	2.80	3.20	97.2	1.80

Key: a) working examples; b) comparative examples; kG) remnant flux density; kOe) coercive field strength; %) degree of orientation

#### [Effects of the Invention]

According to the present invention, it becomes possible to produce W-type hexagonal ferrite magnetic powder by controlling the ambience and temperature in the calcining and heat-treatment steps in a relatively simple manner, and the use of this magnetic powder makes it possible to improve the magnetic characteristics of the plastic magnets used in electrical equipment and the like.